Supporting information

Enhanced Synthetic Access to Tris-CF_3 -Substituted Corroles

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Experimental Section

Chemical and Instrumentation

Pyrrole, Halothane, Sodium Dithionite and PIFA were purchased from Sigma Aldrich. Pyrrole and halothane were passed through neutral aluminium oxide before use. ^1H and ^{19}F NMR spectra were recorded on Bruker Avance III 400 spectrometer (400 MHz for ^1H and 377 MHz for ^{19}F) and chemical shift are reported in ppm relative to residual hydrogen atoms of $CDCl_3$ solvent. HPLC analysis were performed on a combination of JASCO organizer, diode array detector MD-4010, auto sampler AS-4050 and RHPLC pump PU-4180.

Synthesis of 5,10,15-tris(trifluoromethyl)corrole

Procedure A, with isolation of the bilane

The oligomerization step: Sodium dithionite (3 g,15 mmol) and sodium hydrogen carbonate (3.5 g, 42 mmol) were suspended in aqueous acetonitrile solution (H_2O:acetonitrile, 1:2, v/v, 30 mL) in a 250 mL three-necked flask placed in a preheated oil bath (45°C-50°C) fitted with a magnetic bar, thermometer, rubber septum and a reflux condenser connected to an oil bubbler. After increasing the bath temperature to 70°-80° C, a mixture of pyrrole (2.77 mL, 40 mmol) and halothane (3.20 mL, 30 mmol) was injected with a syringe through the septum. Noticeable gas evolution (CO_2) occurred, as the yellow suspension was continually stirred and maintained at 70°-80° for 2h. Progress of the reaction was monitored by HPLC analysis. By the end of the reaction almost all inorganic salts were dissolved. After cooling to room temperature, water (50 mL) was added and the reaction mixture was extracted with diethyl ether (3×30 mL). The organic layer was washed with water and then dried over anhydrous Na_2SO_4. Gentle removal of the solvent on a rotary evaporator provided the oily crude mixture that was separated (silica gel column chromatography) by gradually increasing the amount of DCM (0-100%) in hexane. All the fractions were collected using Erlenmeyer flasks (50 mL) and small amounts from each were added to a test tube for reaction with DDQ, as only fractions containing the bilane become fluorescent upon that treatment. Dipyrromethane[1] was collected from 0-30% DCM/hexane fractions, tripyrromethane from the 30-90% DCM/hexane fractions and tetrapyrrane (bilane) from the 90-100% fractions. Pentapyrrane (a precursor of sapphyrin) was eluted the latest. All products except tripyrrane are liquids. The total amount of isolated tetrapyrrane was 1.5 g, 3 mmol (30% yield).

General reaction conditions for oxidation by PIFA: Bilane (0.5 g, 0.9 mmol) was dissolved in DCM or acetonitrile or propionitrile (200 mL) and purged with Ar gas for 20 min. Then PIFA (1 g, 2.3 mmol) was

added and the reaction was stirred for 2 h at room temperature under an Ar atmosphere. The solvent was evaporated.

H_3(tfc): The purple colored product was purified by column chromatography with an ethyl acetate:hexane (1:9, v/v) mixture as eluent. Yield = 70 mg, 0.14 mmol, 14%. Experiments performed on a five time smaller scale afforded 12-20 mg, 0.02 – 0.04 mmol of $H_3(tfc)^2$ (12-20% yield) from 0.1 g (0.2 mmol) tetrapyrrane.

(tfc)Ga: The crude reaction products were re-dissolved in pyridine (40 mL), a large excess of $GaCl_3$ was added, and the reaction mixture was heated immediately to reflux for 15 min under Ar, followed by evaporation of the solvent and flash chromatography (silica, hexane: DCM: pyridine=85:15:1 -70:30:1). Yield= 80 mg, 0.12 mmol, 14%. Experiments performed on a smaller scale (5x) afforded 20-22 mg, 0.032 - 0.034 mmol of violet pink colored $(tfc)Ga^2$ (17-20% yield) from 0.1 g (0.2 mmol) tetrapyrrane.

(tfc)Mn: The crude reaction mixture was dissolved in 10 mL DMF, then an excess of Mn(II) acetate was added, followed by heating for 1 h under an Ar atmosphere. A silica gel column with 40% DCM in hexane as eluent was used to obtain the product. This reaction, which was only performed on a smaller scale (5x), afforded 12 mg, 0.02 mmol (12% yield) of dark brown solid $(tfc)Mn^2$ from 0.1 g (0.2 mmol) tetrapyrrane.

Procedure B, without isolation of the tetrapyrrane: Halothane (38.5 g, 0.195 mol), pyrrole (14.0 g, 0.209 mol), acetonitrile (80 mL) and water (30 mL) were stirred in an open 250 mL single-necked round-bottomed flask with a portable pH meter probe positioned above the stirbar. The mixture was warmed using a water bath (35-40 °C) and 2 g of $Na_2S_2O_4$ were added in one portion. As the reaction proceeded, the pH of the reaction mixture was maintained between pH 3.5-4.5 by the dropwise addition of a solution of anhydrous sodium carbonate (15.5 g, 0.146 mol) in water (55 mL) from a plastic 60 mL syringe. Three additional 1 g portions of $Na_2S_2O_4$ (5 g total, 0.029 mol) were added to maintain a suitable rate of reaction until all of the base solution had been added over the course of 2-3 h and HPLC analysis (C18, 40-95% ACN/H_2O, 245 nm detection) indicated that the peak corresponding to the tetrapyrrane component corresponded to ~28% of the total integrated area. The reaction mixture was poured into 100 mL of water and 80 mL of 2:1 ether/hexane solution. The layers were separated and the organic layer was washed with brine, dried with magnesium sulfate, and concentrated to afford 23.4 g of the oligomeric mixture. A solution of the crude mixture in acetonitrile (4L) was deaerated at room temperature (bubbling with argon for 5 min) and solid PIFA (46 g, 0.107 mol) was added with stirring. After 16 h, the reaction mixture was evaporated and the residue was dissolved in warm ethyl acetate (160 mL), then diluted with 240 mL of hexane and purified by column chromatography (200 g silica, 65 mm column dia., 40% ethyl acetate/hexane). The corrole-containing fractions were combined and repurified by column chromatography on silica with 25% ethyl acetate/hexane. Recrystallization of the product in two crops from 10% ethyl acetate/hexane afforded H_3(tfc) (0.87 g, 1.7 mmol, 3.3% relative to pyrrole) as dark purple crystals.

HPLC separation conditions of the oligopyrromethanes

HPLC Column details HiCHROM; Cat. Number: LispRP18E-5-250A; Serial Number: LispRP18E-5-2725; Packing: LiChrospher RP18-5 Endcapped; Length: 25 cm; i.d.: 4.6 mm; o.d. ¼”

Test Conditions Mobile phase: Acetonitrile/ water (0.05% Formic acid, 2 mM ammonium acetate); Wavelength: 217 nm; Flow rate: 0.4 mL/min;

Time (min.)	Acetonitrile %	Water % (0.05 Formic acid, 2 mM Ammonium acetate)
0	60	40
10	100	0
12	100	0
12.5	60	40
30	60	40

Table S1. Chemical shifts of H and F atoms in the oligo-pyrromethanes that were isolated from the first step of the reaction depicted in Scheme 2.

	^{1}H NMR							^{19}F NMR	
	C(H)CF_3		β-pyrrole-H		π-pyrrole-H	N(H)		CF_3	
Di-	4.84 (q, 8.8Hz, 1H)		6.21 (m, 2H)	6.25 (m, 2H)	6.77 (m, 2H)	8.10 (br, 2H)		-68.59 (d, 9.1Hz, 3F)	
Tri-	4.77 (q, 8.8Hz, 2H)		6.20 (m, 6H)		6.78 (m, 2H)	8.00 (br, 1H)	8.13 (br, 2H)	-68.67 (d, 9.1Hz, 6F)	
Tetra-	4.68 (q, 7.6Hz, 1H)	4.79 (q, 8.8Hz, 2H)	6.21 (m, 8H)		6.78 (m, 2H)	7.99 (br, 2H)	8.12 (br, 2H)	-68.66 (d, 8.6Hz, 6F)	-68.73 (d, 9.1Hz, 3F)
Penta-	4.71 (q, 8.8Hz, 2H)	4.79 (q, 8.8Hz, 2H)	6.15 (m, 4H)	6.20 (m, 6H)	6.78 (m, 2H)	8.05 (br, 3H)	8.14 (br, 2H)	-68.68 (d, 9.1Hz, 6F)	-68.73 (d, 8.6Hz, 6F)

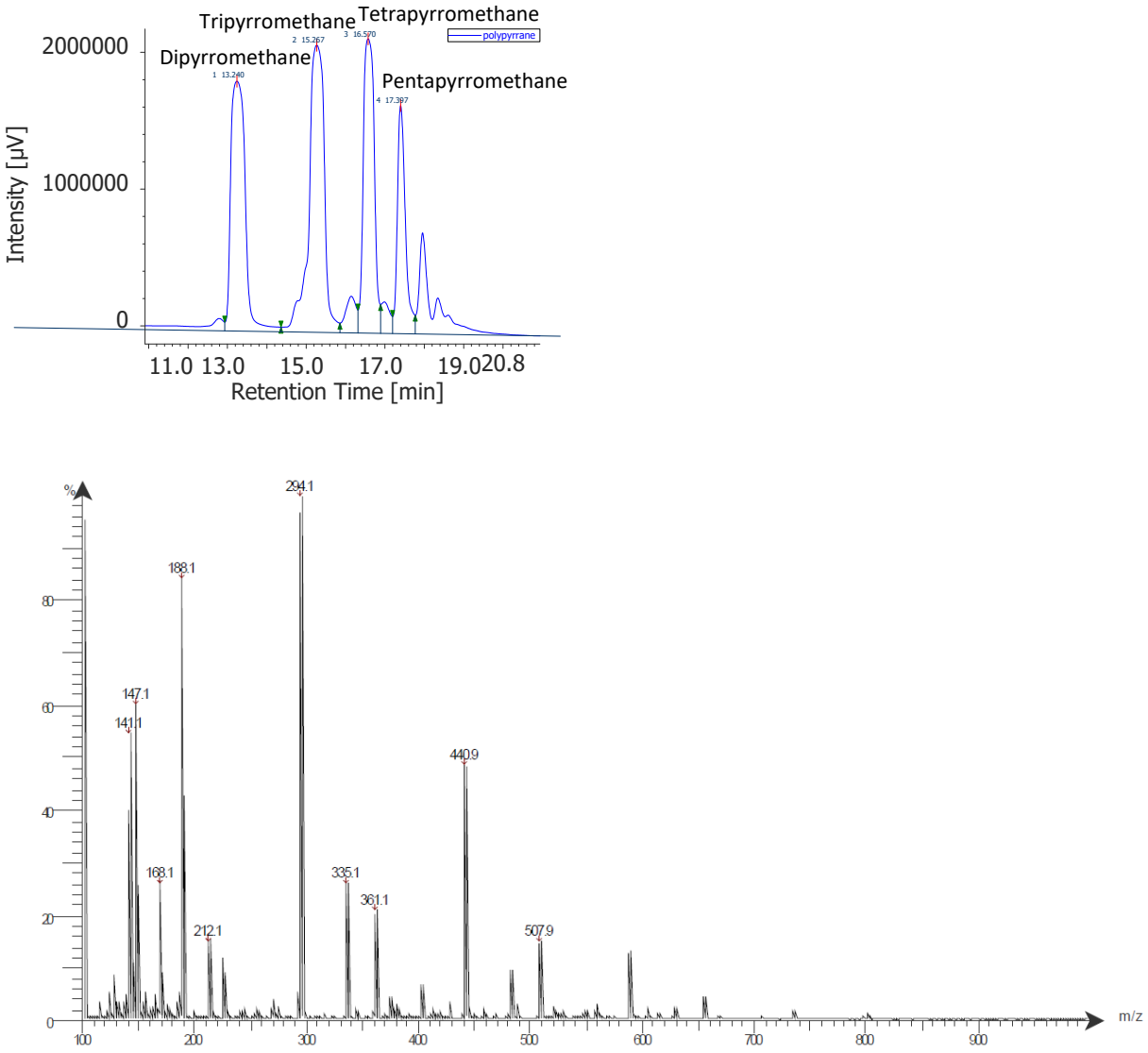

Figure S1. HPLC and HPLC-MS analysis of the oligomeric mixture.

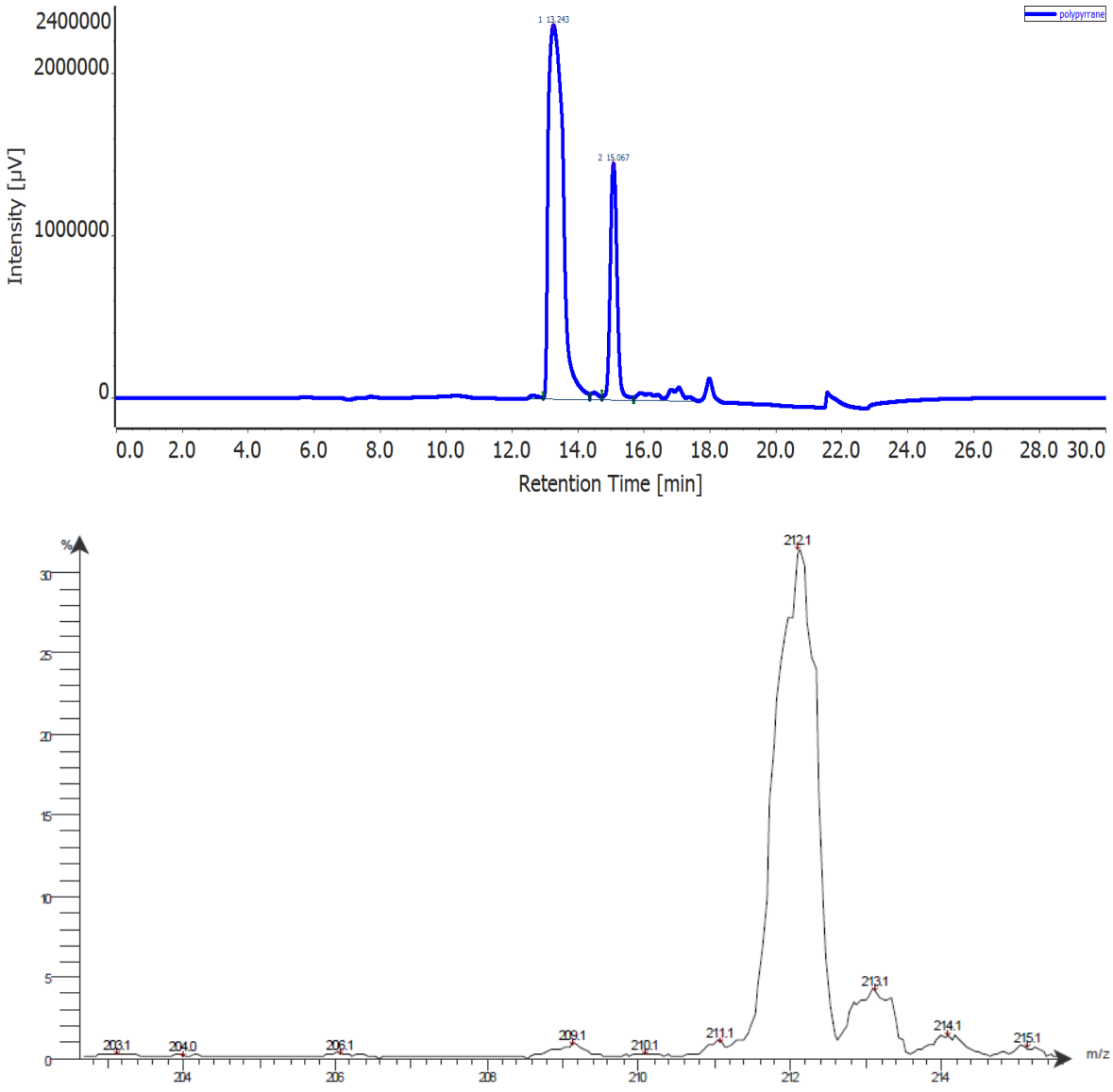

Figure S2. HPLC and HPLC-MS analysis of the dipyrromethane.

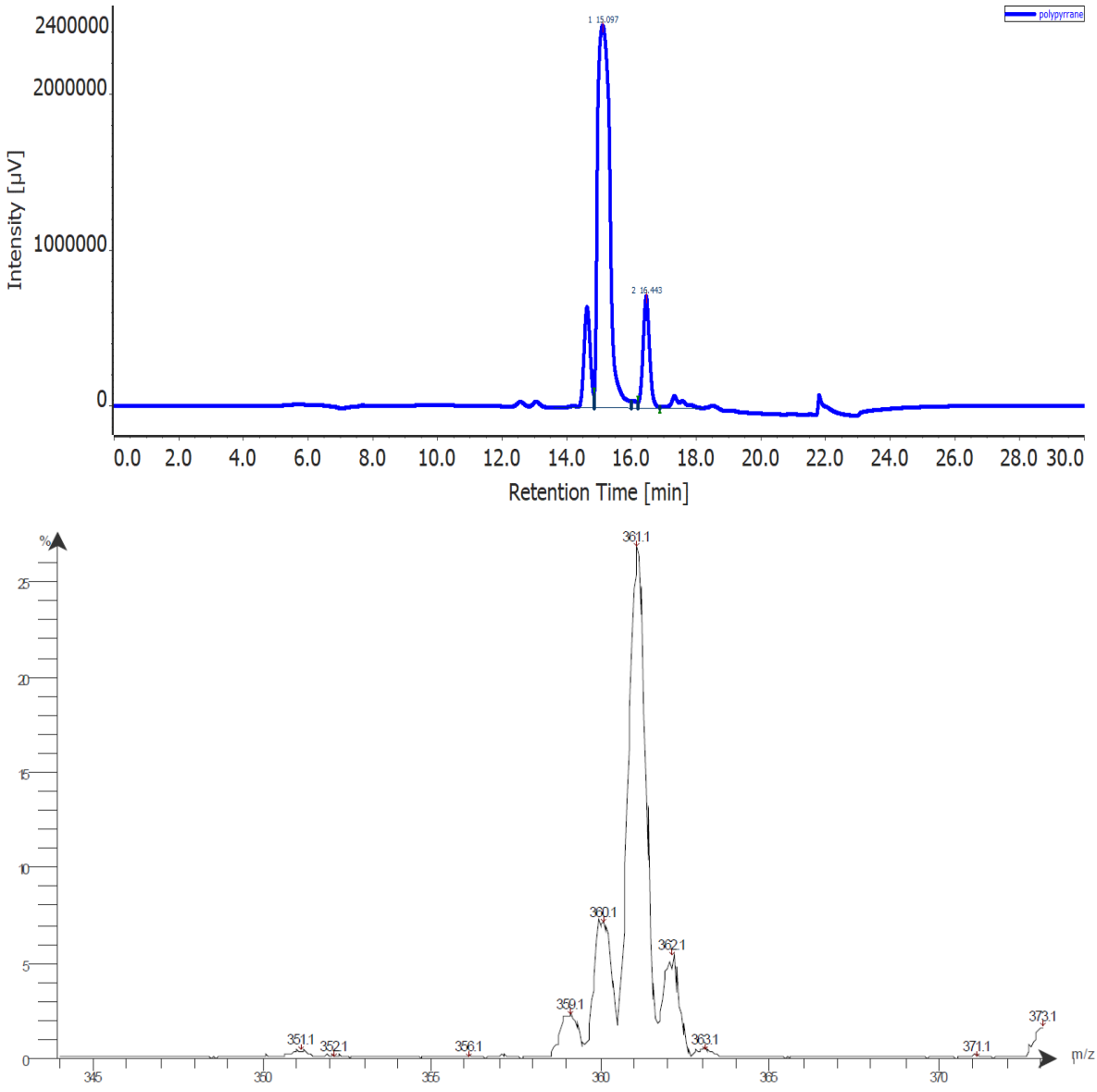

Figure S3. HPLC and HPLC-MS analysis of the tripyrromethane.

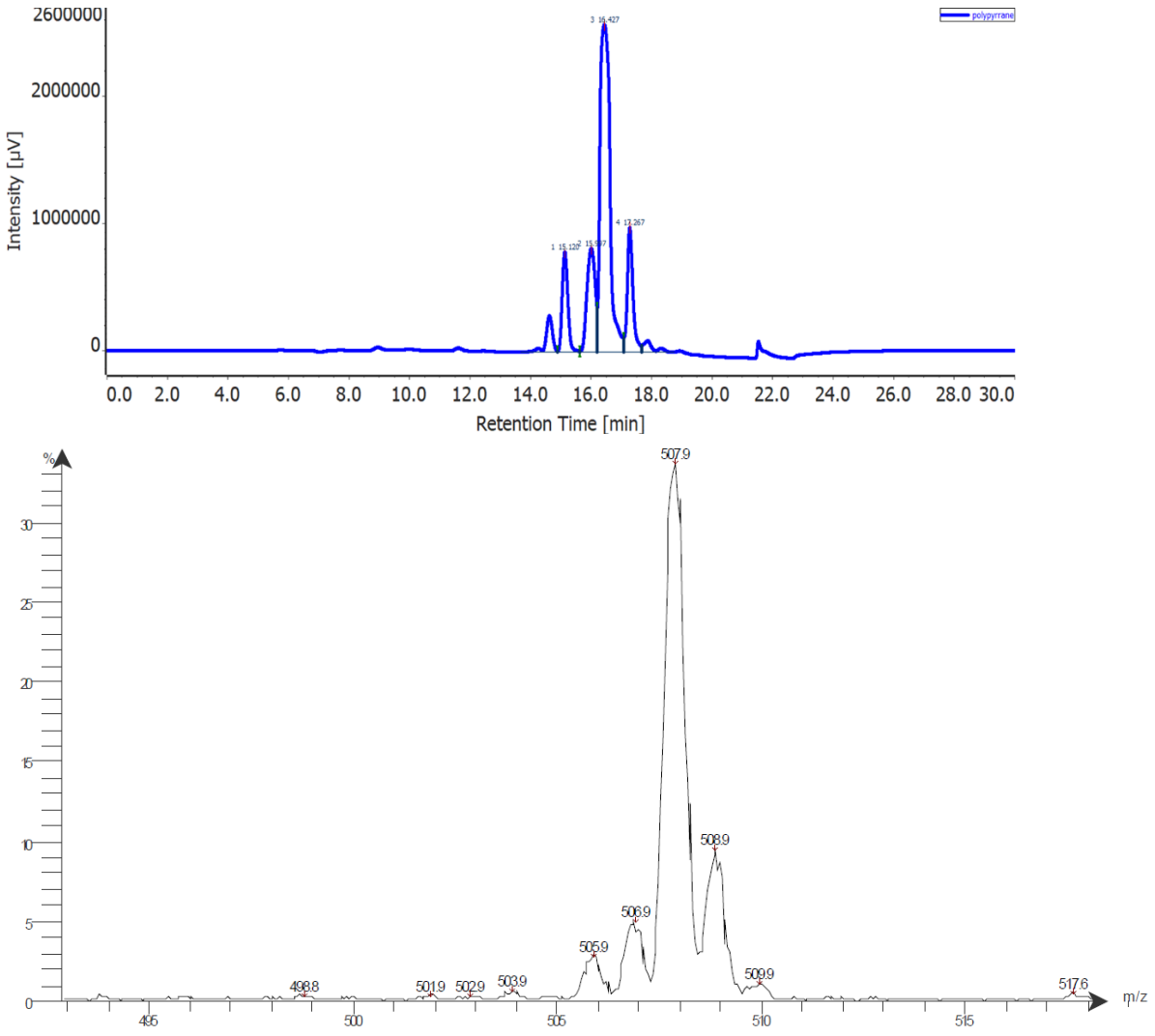

Figure S4. HPLC and HPLC-MS analysis of the tetrapyrromethane.

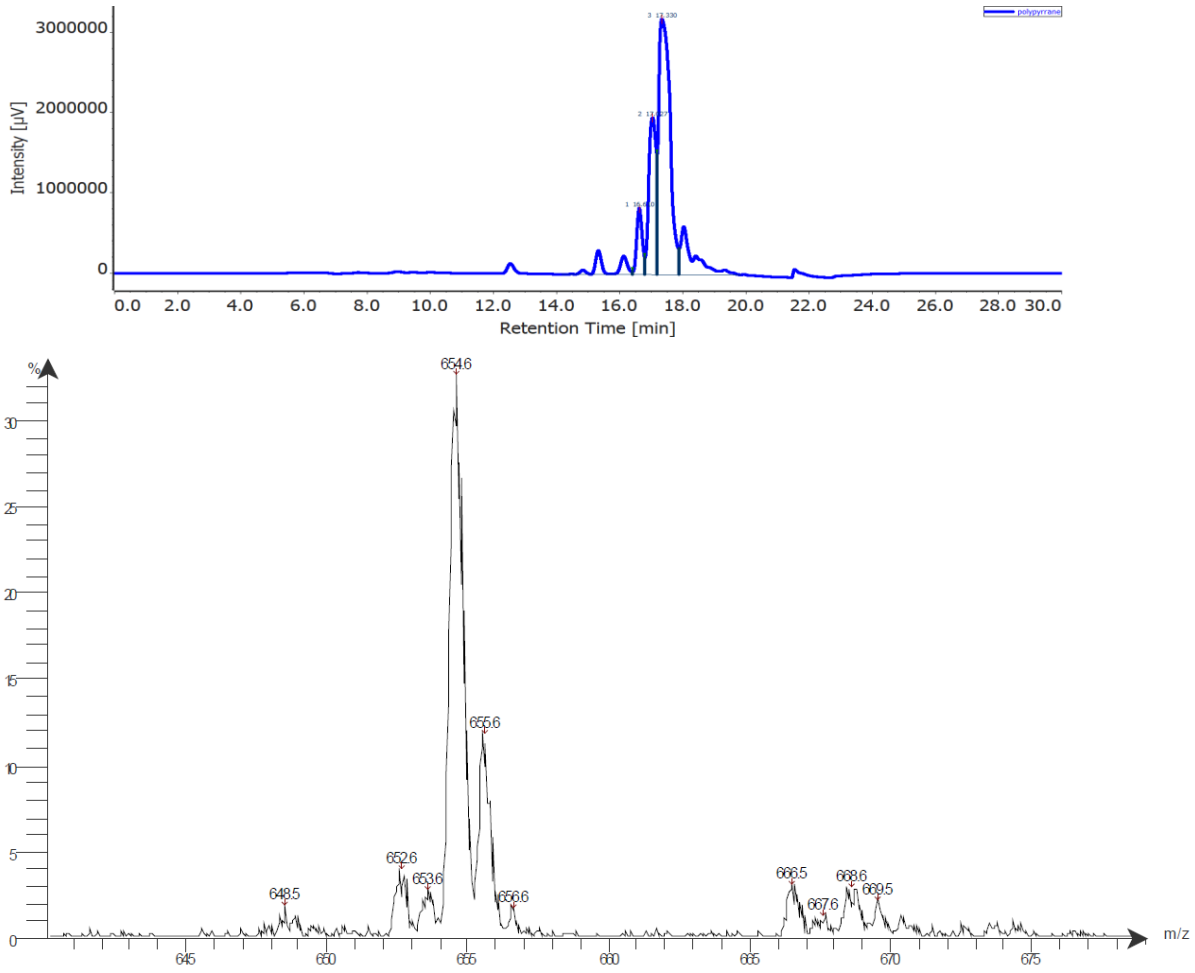

Figure 5. HPLC and HPLC-MS analysis of the pentapyrromethane.

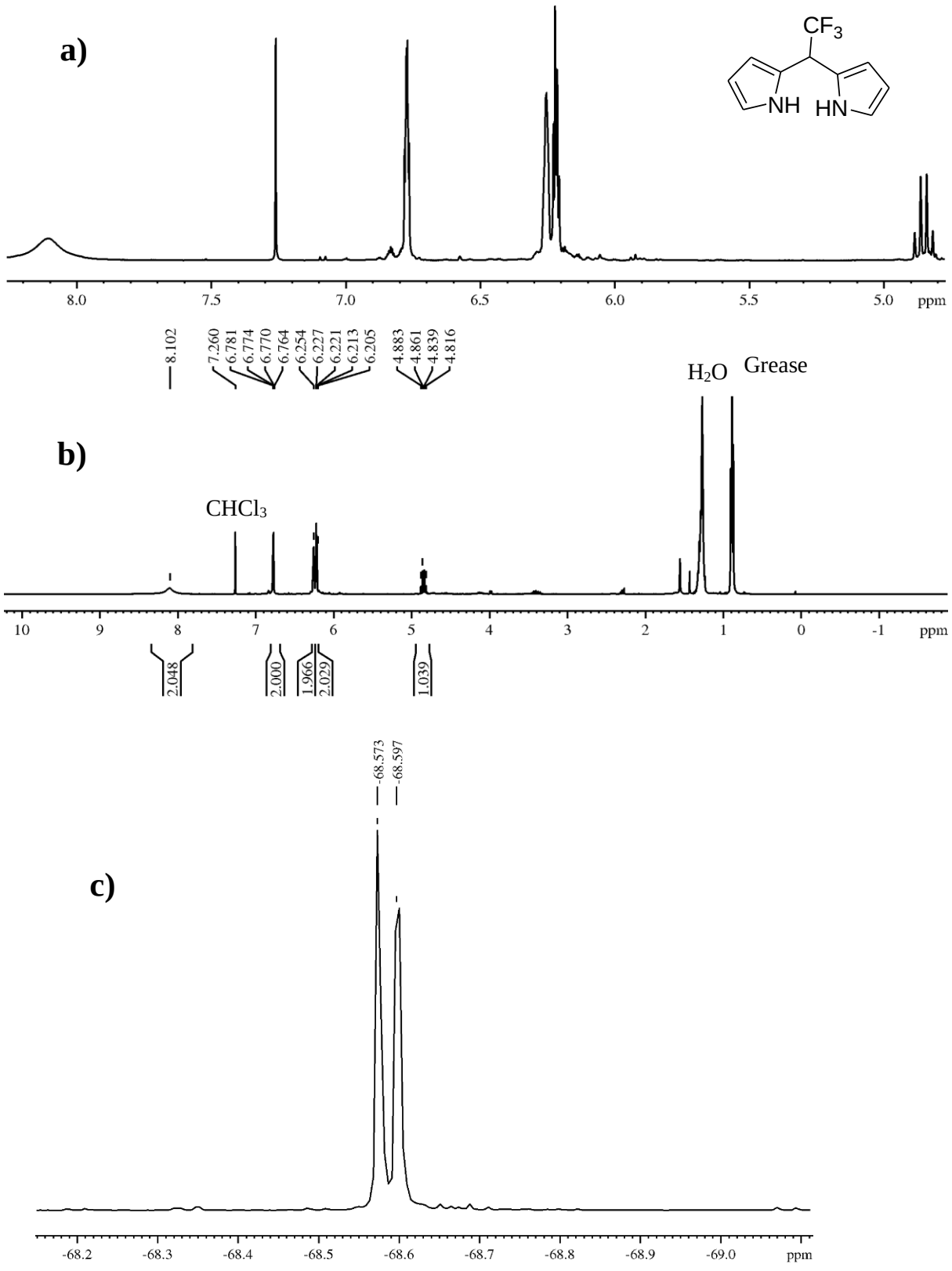

Figure S6. ^{1}H-NMR (400 MHz) (a and b) and ^{19}F-NMR (377 MHz) (c) spectra of the dipyrromethane in $CDCl_3$.

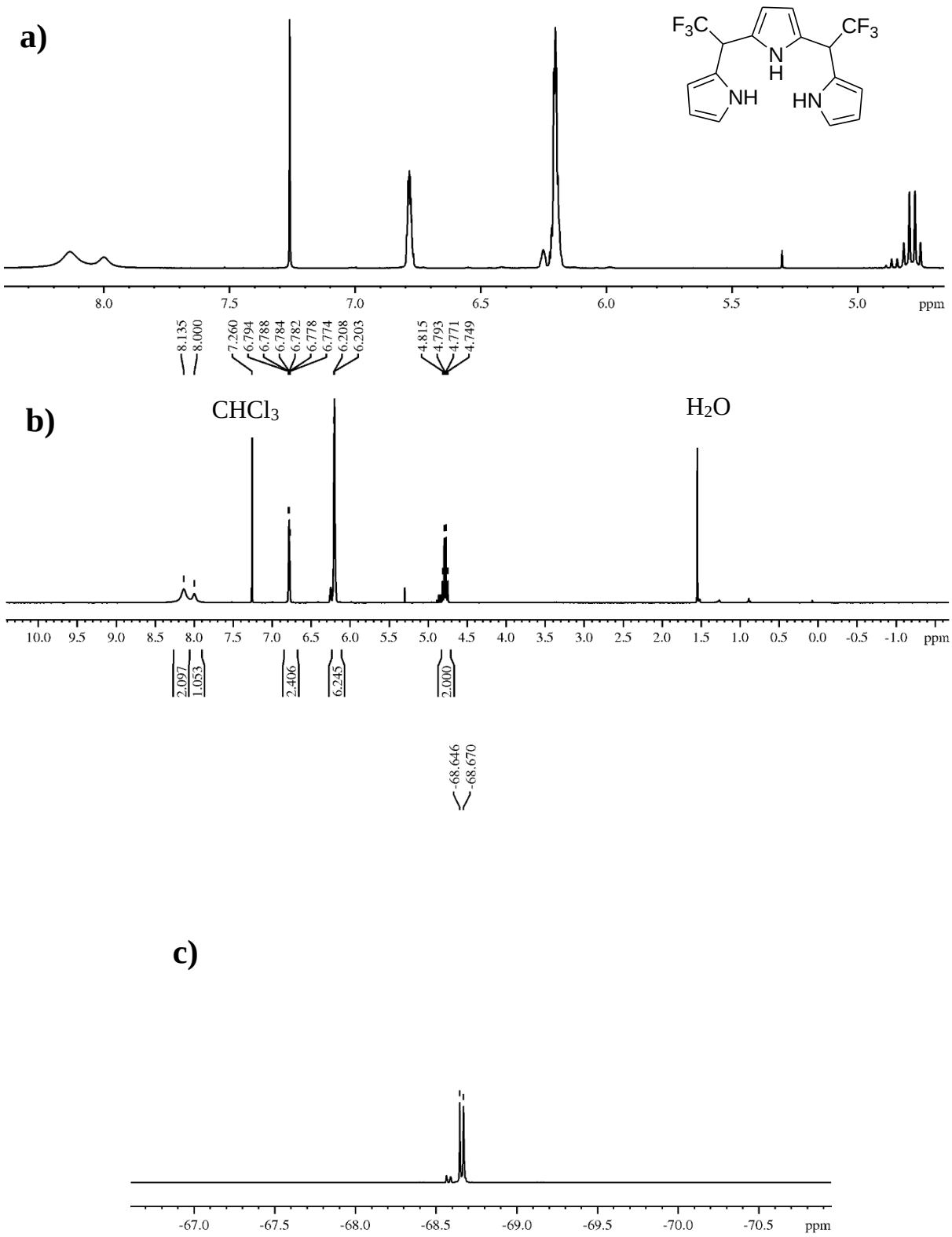

Figure S7. ^{1}H-NMR (400 MHz) (a and b) and ^{19}F-NMR (377 MHz) (c) spectra of the tripyrromethane in $CDCl_3$.

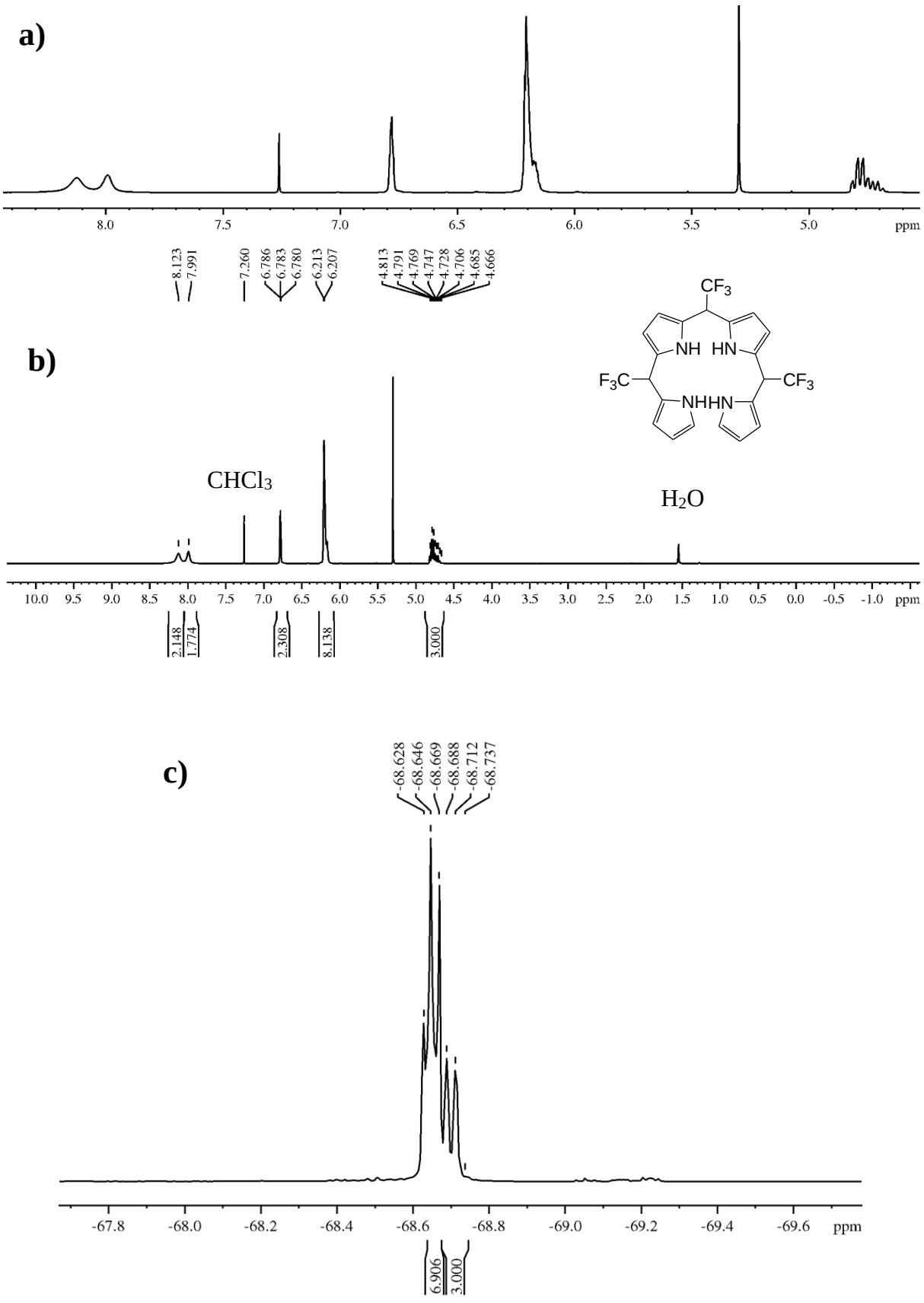

Figure S8. ^{1}H-NMR (400 MHz) (a and b) and ^{19}F-NMR (377 MHz) (c) spectra of the tetrapyrromethane in $CDCl_3$.

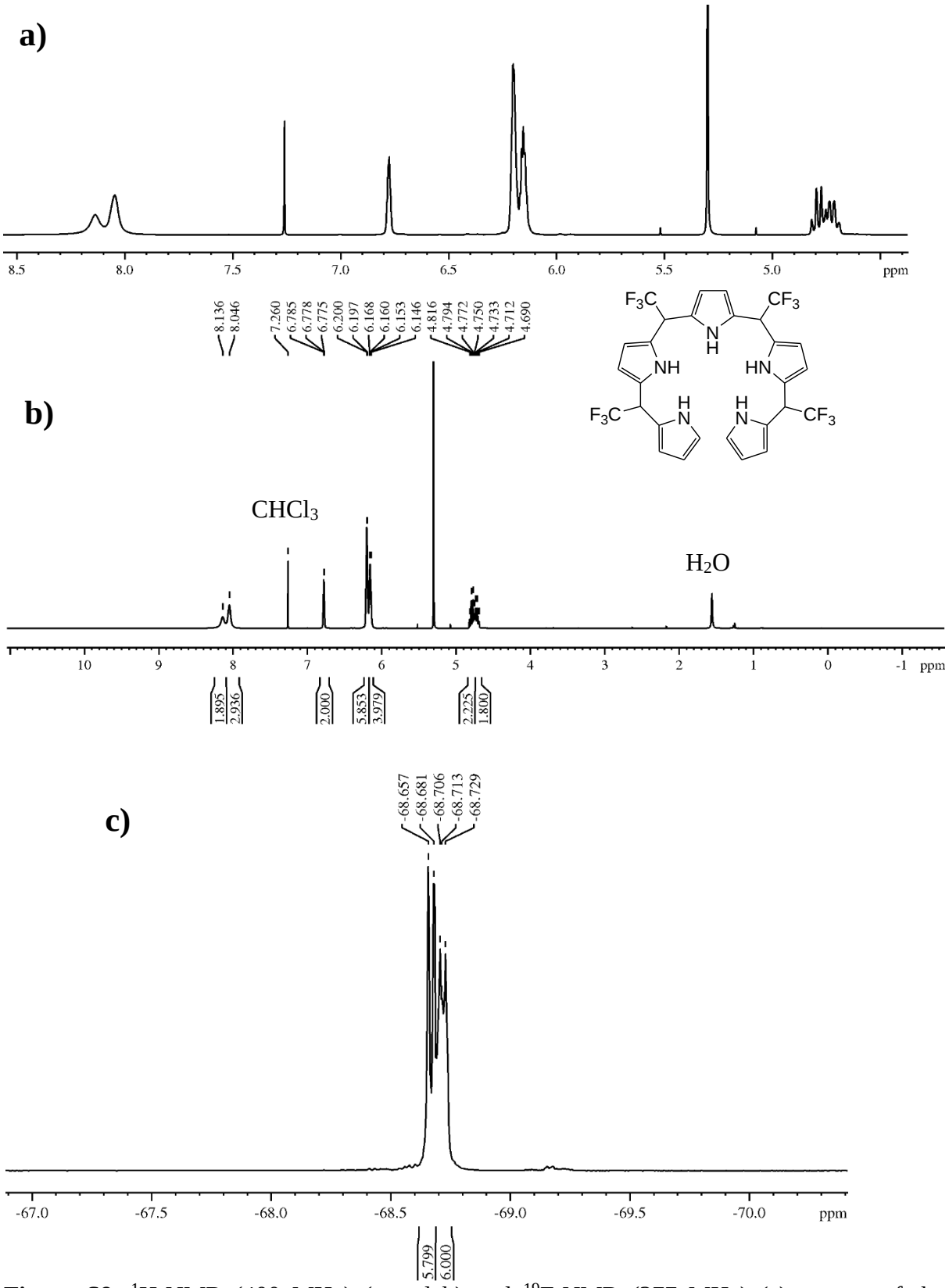

Figure S9. ^{1}H-NMR (400 MHz) (a and b) and ^{19}F-NMR (377 MHz) (c) spectra of the pentapyrromethane in $CDCl_3$.

Reference

(1) Dmowski, W.; Piasecka-Maciejewska, K.; Urbańczyk-Lipkowska, Z. *Synthesis* **2003**, *2003*, 0841.

(2) Chen, Q.-C.; Soll, M.; Mizrahi, A.; Saltsman, I.; Fridman, N.; Saphier, M.; Gross, Z. *Angew. Chem.* **2018**, *130*, 1018.